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RESEARCH ARTICLE

Arsenic Survey in Dried Sediments of Maharlu Saline Lake

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Abstract

Being on the steep slope of Shiraz city and getting the main drainages, Maharlu Lake is always home to extensive levels of urban pollution. Prolonged droughts and drying of surface sediments of the lake usually happen in warm seasons of the year, and with the continuation of the droughts particles spread out from the surface into the surroundings of the lake. Arsenic and its compound are well known for its toxicity and carcinogenicity. Industrial and farming waste in upstream of the lake are the main sources of arsenic and may disperse in Maharlu Lake. In this study, by meshing the lake's surface and by sampling 15 points 3 kilometers away there determined the Arsenic amount. Then, the toxicity indexes and Mueller index together with its risks were studied before zoning of the lake through GIS and verification. The results showed that the average concentration of arsenic was 3.5 mg/ kg of surface sediment. The concentration has gone in most parts of the lake below normal as shown by Mueller index so that its contamination and lower-than-usual toxicity is deemed anthropogenic. Interpolations by GPI, LPI, and IDW methods demonstrated the north part of the lake more concentrated, likely due to the north lake farming and being the entrance of River Soltanabad. The verification of data has recognized the IDW method as the most accurate as regards interpolation. According to the importance of heavy metals in the dust, samples should be taken from winds coming from the lakeside as dust hotspot to control the metals concentration.

Keywords: Arsenic, Maharlu Lake, GIS, Zoning, Mueller index, Toxicity index

1. Introduction

Being on the steep slope of Shiraz city and getting the main drainages, Maharlu Lake is always home to extensive levels of urban pollution. Prolonged droughts and drying of surface sediments of the Lake usually happen in warm seasons of the year, and with the continuation of the droughts particles spread out from the surface into the surroundings of the Lake. Environmental hazards, abnormal decomposition of Arsenic and its transmission along with the particles in micron sizes make the investigation on Arsenic concentration, dispersion, and toxicity a must.

Arsenic is a metalloid element, primarily existing in its inorganic form in water. The toxic impact of arsenic on human health has been documented in numerous studies; to the extent that the International Agency has classified it for Research on Carcinogens (IARC) and the National Toxicity Program (NTP) as a known human carcinogen (WHO, 2012; Department of Health and Human Services, 2011). Apart from its cancerous consequences, long-term exposure to arsenic has been associated with developmental effects, cardiovascular disease, neurotoxicity and diabetes (WHO, 2016). Inorganic arsenic can

easily cross the human and animal placenta and has been reported to increase the risk of adverse pregnancy outcomes such as spontaneous abortion, stillbirth, impaired fetal growth and infant mortality rate (Quansah,2015).

Besides natural pollution from geogenic sources, specific attention has been paid to anthropogenic contribution of As., in certain areas (Fendorf et al., 2010; Moriarty et al., 2014). The primary anthropogenic sources of As including mining, smelting of non-ferrous metals and burning of fossil fuels, use of arsenic-containing pesticides, and use of arsenic in the preservation of timber (Smedley and Kinniburgh, 2002)

The sediments of the seas and the Lakes are frequently the sinks of heavy metals as contaminants, and various studies have proved that these gathering places had much above the allowable limit of contaminants (Aksu et al., 2012; Kishe & Machwa, 2003; Evseev & Krasovskaya, 2015; Fukue et al., 2006).

The studies of Moore et al., 2009 on heavy metals in Maharlu Lake has also shown that the pollution of the water in this regard has been beyond the standard limit, and described Arsenic pollution as an anthropogenic source. Hence, more specific studies on heavy metals as surface sediments toward Maharlu Lake are needed particularly since the beyond standard concentrations of Arsenic in recent years are probable. In this research, keeping the Arsenic threats in view, we study dispersion of this toxic metal in the dried sediment surface of the Lake.

2. Materials and Methods

2.1 Maharlu Lake

Spread about 25000 hectares with a 6×10 km2 dimension, Maharlu Lake is located in 23 km south-east of Shiraz to the west of Lake Bakhtegan, between latitudes 29,19' and 29,31', and between longitudes 52,41' and 52,53'. The water suppliers of this Lake are the rivers and waterways flown to it. The most important to be mentioned are Khosk (dry) River, Chenar-e Rahdar River, Nazarabad River, and Soltanabad River (see Fig. 1). A few springs of water also enter the Lake. Maharlu Lake is the easternmost part of the Shiraz plain with very salty water and is considered as one of the enormous deposits of salt in Iran. Salt procession from this Lake is performed by the Salt Extraction Complex affiliated to Shiraz Petrochemical Company. Villages and agricultural lands surround Maharlu Lake, and on account of inflow of Khoshk River which passes through the city of Shiraz leading to the Lake and is a seasonal river pestered by various kinds of household, commercial, industrial, and agricultural wastewaters, the quality of its water much affects on the Lake with regard to heavy metals pollution.

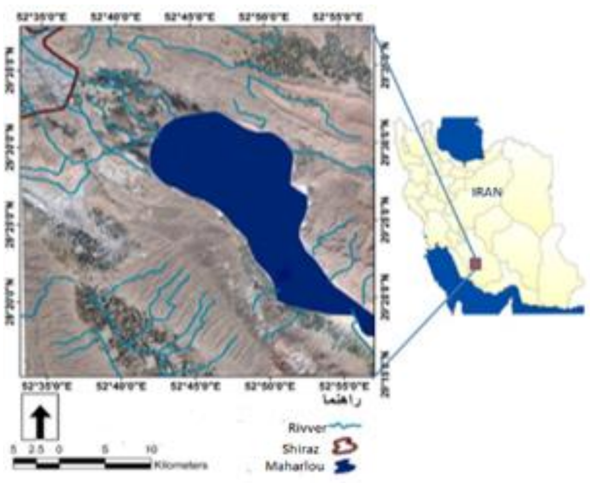

Fig.1. Location of Saline Maharlu Lake

2.2 Sampling

The samplings were performed in summer 2015. Since the aim of the research was an investigation of likelihood of heavy metals dispersion by dust during the dryness of the Lake, the samples were taken from the surface of the Lake sediments. The number of sampling points was 15 for the selection of which the Lake was divided by meshes 3 kilometers away from each other in order for all areas to be sampled. Afterward, the geographical coordinates of the selected points in the provided map were determined via Google Earth software. Then, using GPS, the points were spotted on the Lake. It was tried that the samples be taken of a one square meter surface. The full dryness of the Lake was conducive to having access to all points. Fig. 2 shows the sampling locations, and Table 1 contains the coordinates of the sampled points.

2.3 Experiments to determine concentrations of Arsenic

After the samples were dried in Desiccator, they were digested in acid, and then all Arsenic in the samples (not only soluble metals) were measured using atomic absorption system. The test method was done according to as Journal 893 of Institute of Water and Soil Research

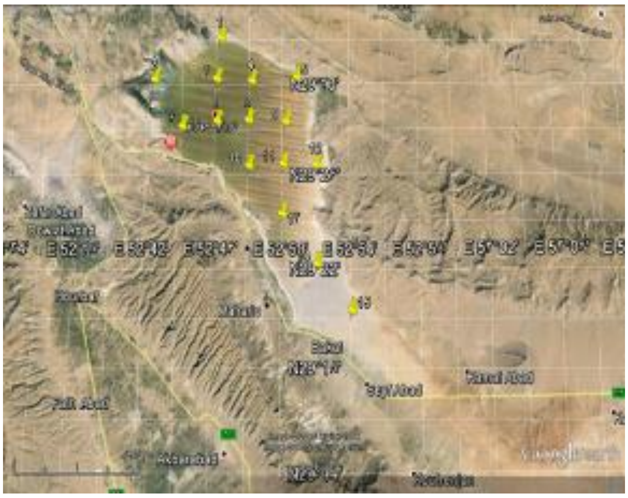

Fig. 2. Sampling locations in Saline Maharlu Lake

Table 1. coordinates of the sampled points.

Location	Coordinate X	Coordinate Y
Station 1	29.52089	52.769514
Station 2	29.49751	52.720733
Station 3	29.29798	52.766449
Station 4	29.49654	52.801394
Station 5	29.49886	52.846025
Station 6	29.46656	52.733275
Station 7	29.46736	52.767336
Station 8	29.65906	52.798644
Station 9	29.43386	52.835439
Station 10	29.43531	52.799764
Station 11	29.39947	52.833225
Station 12	29.39947	52.832653
Station 13	29.36453	52.866639
Station 14	29.33249	52.899494

2.4. The method of analyzing the results

2.4.1. Comparison with Geochemical Criteria

Håkanson designated the geochemical criteria such as enrichment factor (EF) and Mueller index (Igeo), 1980 as the main computation indices to evaluate contamination of sediments. The Mueller index was calculated from the following relation (Moore et al., 2009):

$$Igeo=\log 2[Cn/1.5Bn] \qquad (1)$$

In which Cn is the concentration of the tested pollutant, and Bn is the background pollution of the same pollutant before pollution, and the references usually use the average global shale as regards (Turekian & Wedepohl, 1961), and some use the highest concentration of earth crust (Taylor & Mclennan, 1985). The average concentration of Arsenic in global shale is equal to 0.3 ppm (kabata-Pendias & Mukherji, 2007). However, not all of these world standards could be applied in the local areas (Dekov et al., 1998; Roussiez et al., 2005).

In the studies conducted by Moore et al. (2009) in Maharlu region, the local background values for arsenic was equal to the average global ones. The obtained values were compared with those of the references. Table 2 shows the classification and the annotations of Mueler land accumulation index.

2.4.2. Evaluation of Toxicity for Ecosystem

To evaluate the toxic effects of the heavy metals on the environment, the obtained results were compared with the sediment quality guidelines (SQGs) (McDonald et al., 2000). The values of SQGs are the determiners of Threshold Effect Level (TEL). This level for Arsenic is equal to 5.9, for evaluation of the effect in the ecosystem.

2.4.3 Drawing of Geo statistic and Zonings Data Using ArcGIS

Interpolation methods for preparing the GIS maps are helpful method for analyzing dispersion pollutant in water, soil and air (Dehghani, 2013; Dehghani, 2014)

1. Method of inverse distance raised to the power of 2 (IDW)
2. LPI. methods
3. GPI. methods

2.5. Method of Verification Evaluation

To choose a suitable way for interpolation the method of reciprocal evaluation was adopted. In this method, an observed point is removed in each stage and then its value is estimated by the other observed points. This process is repeated for all observed points so that ultimately there would exist estimates the same number of observed points. Having the real estimated values, one could obtain the error as well as the deviation of the method. In this research, to find the best interpolation way, the root-mean-square-error measure is used.

Table 2. Classification and the annotations of Mueller land accumulation index.

Designation of sediment quality	Mueler land accumulation index
Uncontaminated	0
uncontaminated to moderately contaminated	0-1
moderately contaminated	1-2
moderately to strongly contaminated	2-3
strongly contaminated	3-4
strongly to extremely contaminated	4-5
extremely contaminated	5<

Table 3. classification and the annotations of Mueller land accumulation index.

Statistical indexes	Arsenic
min (mg/kg)	0.36
max(mg/kg)	6.31
average (mg/kg)	3.52
Standard division	1.54

Table 4. Mueller index and toxicity for Arsenic concentration in sampling places

No of station	TEL	Muler class (Table2)	Muler index	Arsenic (mg/kg)	Level of Toxicity
1	5.9	ZERO	-4.437405312	0.9	nontoxic
2	5.9	ZERO	-1.607330314	6.4	toxic
3	5.9	ZERO	-5.799975392	0.35	nontoxic
4	5.9	ZERO	-1.963474124	5	nontoxic
5	5.9	ZERO	-1.99262047	4.9	nontoxic
6	5.9	ZERO	-4.519867472	0.85	nontoxic
7	5.9	ZERO	-5.285402219	0.5	nontoxic
8	5.9	ZERO	-2.099535674	4.55	nontoxic
9	5.9	ZERO	-1.906890596	5.2	nontoxic
10	5.9	ZERO	-1.8259706	5.5	nontoxic
11	5.9	ZERO	-2.007417472	4.85	nontoxic
12	5.9	ZERO	-1.736965594	5.85	nontoxic
13	5.9	ZERO	-1.99262047	4.9	nontoxic
14	5.9	ZERO	-3.799975392	1.4	nontoxic
15	5.9	ZERO	-4.147898695	1.1	nontoxic
Average	5.9	ZERO	-2.46982679	3.52	nontoxic

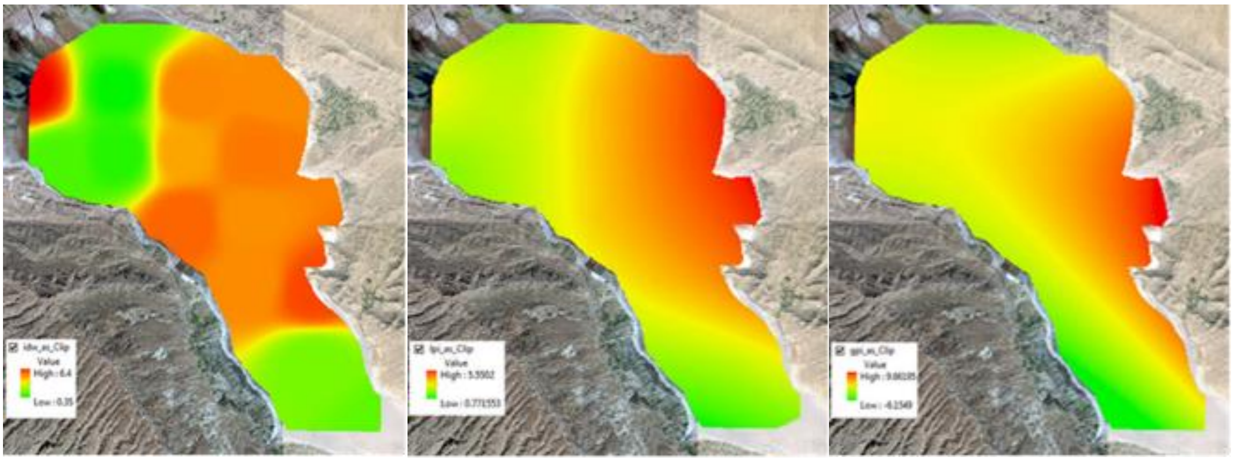

Fig.3. Geostatistical Interpolation in Research area. (left) Inverse Distance Weighting, (middle) LPI Interpolation, and (right) GPI Interpolation.

3. Results and Discuss

3.1. Geochemical Indexes and Environmental toxicity

The calculated of Mooler indexes in various sampling stations are listed in table 4. As the fourth column of table 4 is shown, Theses indexes in all stations are lower than zero and about table2, all stations are ranked in zero class and it indicates that concentration As is not a contaminant in all stations.

On Table 4, also compare the As Concentration to the TEL these results showed that the Arsenic concentration is upper than TEL only in the station 2 and in the other stations it is lower than TEL. The concentration of Arsenic in station 2 is toxic for animates. The station 2 is located in the entrance of Soltanabad river to the lake. In this part of the lake, the sedimentation of particles happened. Moreover, all of the pollutants that have been absorbed in particulate materials, such as, mud and clay settle in this part.

As concentrations are shown from high to low by colors. The highest concentration is shown by red and lowest one is shown with green color. Interpolation with the IDW method as showed that the higher concentration belongs to the south-west of the lake that is located in the entrance of Soltanabad River. This part is a landform that forms from the deposition of sediment carried by the Soltanabad *river* as the flow leaves its mouth and enters slower-moving or stagnant water. As IDW interpolation shown another part of the lake in the middle, it is red. There are many garden and farms in the north and south of the lake. Arsenic compounds are using in some fertilizer and poisonings. The run-off from these forms may be a reason for increasing the arsenic in the middle part of the lake. Albeit, As. Concentration in this part is not reached to the toxic limit.

The interpolation with the LPI method showed that the higher concentration belonged only to the middle part of the lake. In this method of interpolation, the single points of high concentration of pollutant are neglected. The result of interpolation with the GPI method is quite similar with LPI methods.

3.3 Data Verifications

the verifications of various geo-statistic methods using the least average squares approach (table 6). This table is shown that interpolation with the IWD method is more real than other methods.

Table 6. verifications of various geo-statistic methods using the least average squares approach.

Parameter	IDW	LPI	GPI
As	2.104574	2.638558	2.990969

RMS – root mean square

4.Conclusion

The average concentration of arsenic is 3.52mg/kg of surface sediment. The investigations on arsenic concentration in surface sediments done by Moore et al. in 2009 have shown the average concentration as 0.52 mg/kg. Attesting that the arsenic level has been increased during the 5 year interval between the two studies, and it may increase dramatically in following years, so it needed to more notice to Arsenic source in farming and industrial waste and wastewater.

The results also show that the Uncontaminated of arsenic in many stations, based on Mueller index is perceived. In only one station, arsenic is above the minimum level for creating toxicity in the sediments. One of the reasons of low concentration of arsenic in the lake sediments may be regarding to high adsorption capacity of clay particles in the run-off path. These particles are settled before receiving to the lake.

The interpolations performed by GPI, LPI and IDW methods show the north and west parts of the Lake heavier in concentration due to being affected by the farming in north of the Lake as well as by the entrance of Soltanabad River. Also, data verification highlights IDW as the most accurate interpolation method. According to the significance of heavy metals in the dust, samples should be taken from winds blowing from the Lakeside as dust hotspot to control the metals' concentration. Given of the results on hand and knowing the way the heavy metals enter into the Lake, it is suggested that use of chemical fertilizers and toxins be controlled particularly on edge and at the basin of the Lake, mainly in the agricultural areas due north.

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